

Chapter 1

INTRODUCTION

1.1 Naphtha

Naphtha is transformed into reformat by catalytic reforming. This process involves the reconstruction of low-octane hydrocarbons in the naphtha into more valuable high-octane gasoline components without changing the boiling point range. Naphtha and reformat are complex mixtures of paraffins, naphthenes, and aromatics in the C₅ -C₁₂ range, naphtha composition. Paraffins or alkanes are saturated aliphatic hydrocarbons with the general formula C_nH_{2n+2}. They are either straight-chain (n-paraffins) or branched structures (i-paraffins). The boiling point increases by about 25-30°C for each carbon atom in the molecule, and the boiling point of an n-paraffin is always higher than that of the i-paraffin with the same carbon number. The density increases with increasing carbon number as well. Olefins or alkenes are unsaturated aliphatic hydrocarbons. Like the paraffins, they are either straight chains or branched structures, but contain one or more double bonds. Mono-olefins have the general formula C_nH_{2n}. Naphthenes or cycloalkanes are saturated cyclichydrocarbons that contain at least one ring structure. The general formula for mononaphthenes is C_nH_{2n}. The most abundant naphthenes in petroleum have a ring of either five or six carbon atoms. The rings can have paraffinic side chains attached to them. The boiling point and the density is higher than for any paraffin with the same number of carbon atoms. Aromatics have the general formula C_nH_{2n-6} and contain one or more polyunsaturated rings (conjugated double bonds). These benzene rings can have paraffinic side chains or be coupled with other naphthenic or aromatic rings. The boiling points and the densities of these polyunsaturated compounds are higher than that of both paraffins and naphthenes with the same carbon number. The reactivity of the unsaturated bonds make the C₆, C₇, and C₈ aromatics or BTX (benzene, toluene, xylenes) important building blocks for the petrochemical industry, Aromatics have high octane numbers. The composition of a given naphtha depends on the type of crude oil, the boiling range of the naphtha, and

whether it is obtained directly from crude oil distillation or produced by catalytic or thermal cracking of heavier oil fractions. A typical straight-run medium naphtha contains 40 - 70 wt % paraffins, 20 -50 wt % naphthenes, 5 - 20 wt % aromatics, and only 0 - 2 wt % olefins. Naphtha produced by fluid catalytic cracking (FCC), coking, or visbreaking may contain 30 - 50 wt % olefins

Table 1 The feed composition of catalytic reforming unit

Naphtha composition	Volume [%]
Hydrogen	0.0
Methane	0.0
Ethane	0.0
Propane	0.0
Isobutane	0.0
N-Butane	0.0
C ₅ -Paraffins	0.0
C ₆ -C ₇ -C ₈ -C ₉ -C ₁₀ -C ₁₁ Paraffins	56.3
C ₆ -C ₇ -C ₈ -C ₉ -C ₁₀ -C ₁₁ Naphthenes	31.2
Benzene,Toluene,C ₈ -C ₉ -C ₁₀ -C ₁₁ Aromatics	12.5
Total	100.0

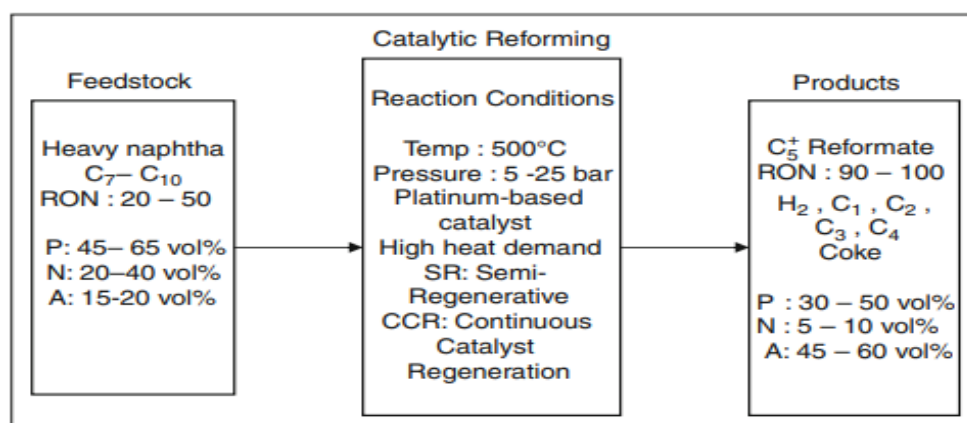
1.2 Catalytic Reforming

Catalytic reforming is the process of transforming C7–C10 hydrocarbons with low octane numbers to aromatics and iso-paraffins which have high octane numbers. It is a highly endothermic process requiring large amounts of energy. A schematic presentation of the feedstock, products and process condition is shown in Figure 1.1. The process can be operated in two modes: a high severity mode to produce mainly aromatics (80–90 vol%) and a middle severity mode to produce high octane gasoline (70% aromatics content).

1.2.1 Reformer Feed Characterization

Feeds are characterized by the Watson characterization factor (K), naphthenes (N) vol% and aromatics (A) vol% in which ($N \geq 2A$) must be defined. In addition, initial boiling points (IBP) and end points (EP) for feeds must be characterized. Feeds can be also characterized by the hydrocarbon family and their number of carbon atoms. Naphthenic feeds give a much higher yield than paraffinic feeds. The main feed comes from hydrotreated heavy naphtha, and some feed comes from hydrotreated coker naphtha.

Figure 1.1 catalytic reforming process



1.2.2 Role of Reformer in the Refinery and Feed Preparation

The catalytic reformer is one of the major units for gasoline production in refineries. It can produce 37 wt% of the total gasoline pool. Other units such as the fluid catalytic cracker (FCC), the methyl ter-butyl ether (MTBE) production unit, alkylation unit and isomerization unit, also contribute to this pool. These units will be covered in other chapters of the book. The straight run naphtha from the crude distillation unit is hydrotreated to remove sulphur, nitrogen and oxygen which can all deactivate the reforming catalyst. The hydrotreated naphtha (HTN) is fractionated into light naphtha (LN), which is mainly C5–C6, and heavy naphtha (HN) which is mainly C7–C10 hydrocarbons. It is important to remove C6 from the reformer feed because it will form benzene which is considered carcinogenic upon combustion. Light naphtha (LN) is isomerized in the isomerization unit (I). Light naphtha can be cracked if introduced to the reformer. The role of the heavy naphtha (HN) reformer in the refinery is shown in Figure 1.2. Hydrogen, produced in the reformer can be recycled to the naphtha hydrotreater, and the rest is sent to other units demanding hydrogen

1.2.3 Research Octane Number

The research octane number (RON) is defined as the percentage by volume of iso-octane in a mixture of iso-octane and n-heptane that knocks with some intensity as the fuel is being tested. A list of the RON of pure hydrocarbon is given in Appendix D. It is seen from this appendix that the RON of paraffins, iso-paraffins and naphthenes decrease as the carbon number of the molecule increases. Aromatics have the opposite trend. This is shown in Figure 1.3.

Figure1.2 Role of reformer in refinery

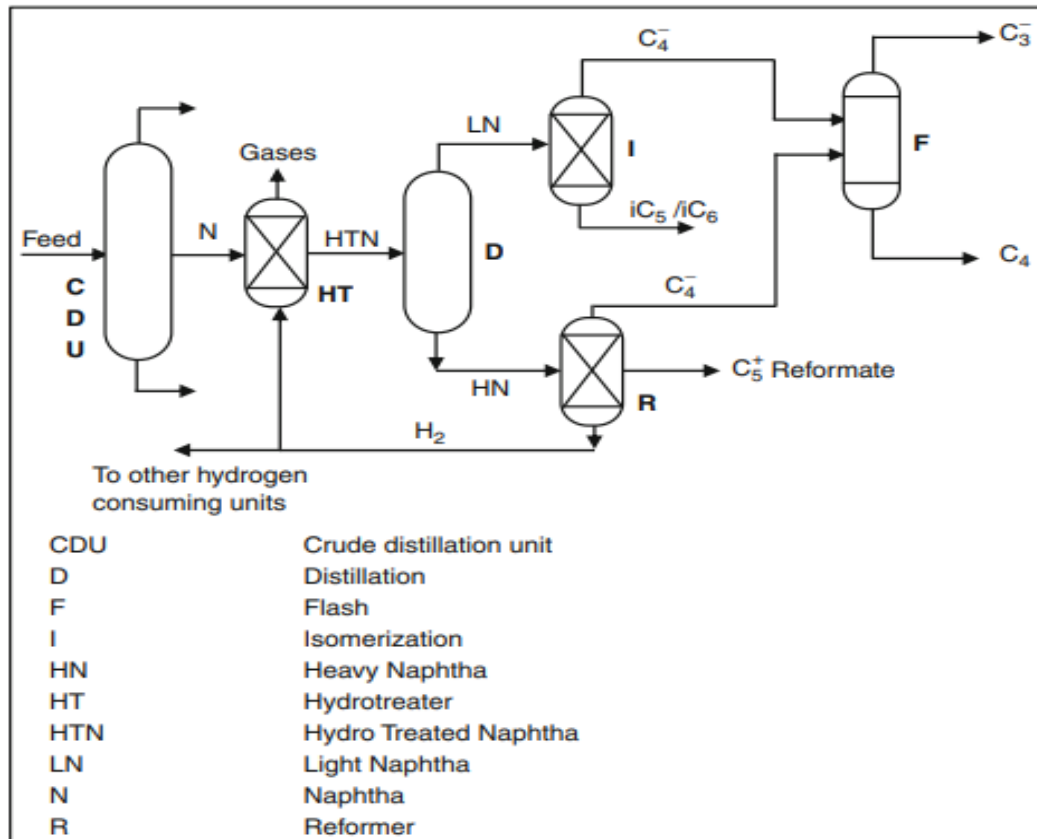
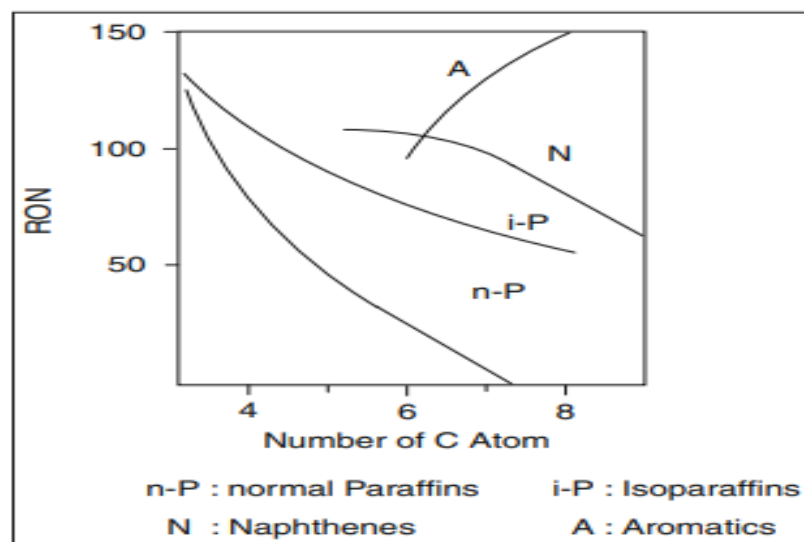
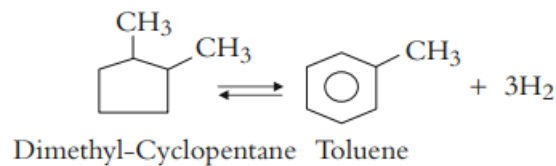
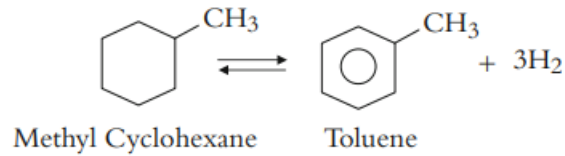


Figure1.3 Variation of research octane number(RON)

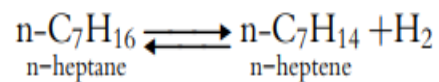


1.2.4 Reforming Reactions

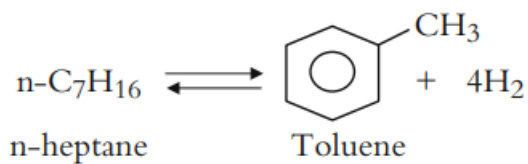
1.2.4.1 Naphthene Dehydrogenation of Cyclohexanes



1.2.4.2 Paraffin Dehydrogenation

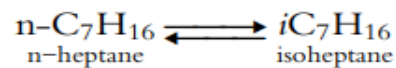


1.2.4.3 Dehydrocyclization



All the above reactions are highly endothermic.

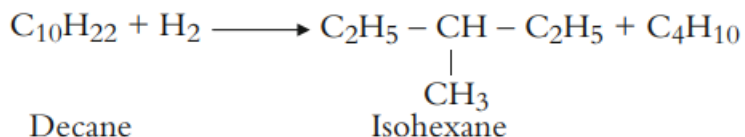
1.2.4.4 Isomerization



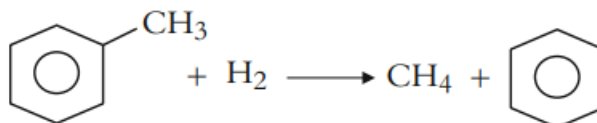
Isomerization is a mildly exothermic reaction and leads to the increase of an octane number

1.2.4.5 Hydrocracking Reactions

Hydrocracking reactions are the main sources of C4 hydrocarbons (C1 , C2 , C3 and C4). The reactions are highly exothermic and consume high amounts of hydrogen. Cracking results in the loss of the reformat yield. Paraffin hydrocracking.



Hydrocracking of aromatics

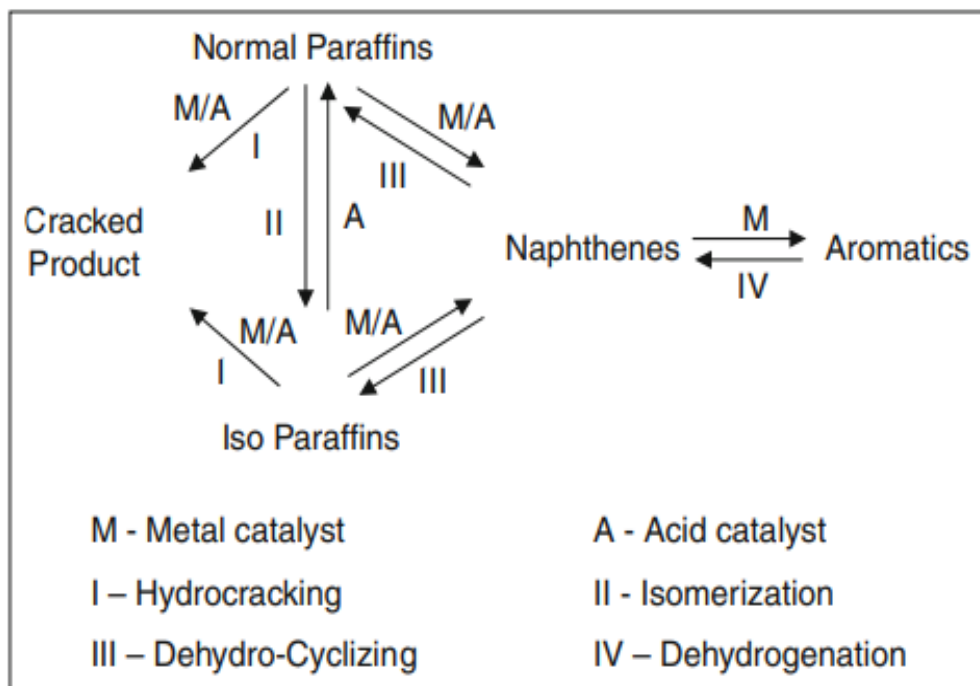


Other paraffins can crack to give C₁–C₄ products.

1.2.4.6 Coke Deposition

Coke can also deposit during hydrocracking resulting in the deactivation of the catalyst. The catalyst in this case has to be re-activated by burning off the deposited coke. The catalyst is selected to produce a slow hydrocracking reaction. Coke formation is favoured at low partial pressures of hydrogen. Hydrocracking is controlled by operating the reaction at low pressure between 5–25 atm (74–368 psia), not too low for coke deposition and not too high in order to avoid cracking and loss of reformat yield. A summary of reformer reactions and interactions is shown by the reaction network in Figure1.4

Figure1.4 Network of reforming reaction



1.2.5 Thermodynamics of Reforming Reactions

The dehydrogenation reactions are the main source of reformate product and are considered to be the most important reactions in reforming. These are highly endothermic reactions and require a great amount of heat to keep the reaction going. For this reason three reactors are usually used in the reforming process with heating the product from each reactor before entering the other.

The dehydrogenation reactions are reversible and equilibrium is established based on temperature and pressure. It is usually important to calculate the equilibrium conversion for each reaction. In reforming, a high temperature around 500C (932F) and a low hydrogen pressure are required. The minimum partial pressure of hydrogen is determined by the amount of the desired aromatics conversion

1.2.6 Reaction Kinetics and Catalysts

The catalyst used for reforming is a bifunctional catalyst composed of platinum metal on chlorinated alumina. Platinum acts as the centre for the dehydrogenation reaction, and chlorinated alumina acts as an acidic site to promote structure changes, such as cyclization of paraffins and isomerization of the naphthenes. Recently additional elements have been added to platinum to promote additional properties for the catalyst. Iridium (Ir) is added to boost activity, Rhenium (Re) is added to operate at lower pressures and Tin (Sn) is added to improve yield at low pressures. The use of Pt/Re is now most common in semi-regenerative (SR) processes with Pt/Sn is used in moving bed reactors. The quantity of chlorine used is approximately 1 wt% of the catalyst and the quantity of platinum is from 0.2 to 0.6 wt%. Impurities that might cause deactivation or poisoning of the catalyst include: coke, sulphur, nitrogen, metals and water. Because of these problems, the reformer feed has to be severely hydrotreated to remove most of these impurities, and the reformer should be operated at high temperature and low pressure to minimize coke deposition. Paraffin and naphthene dehydrogenation reactions are very rapid and usually occur in the first reactor. The isomerization of paraffin and naphthenes is fast, whereas hydrocracking is slow and takes place in the last reactor. The effect of operating conditions on reaction rate and other properties is shown in Table 1.2

1.2.7 Process Technology

There are several commercial processes available for reforming. These include Platforming (UOP), Powerforming (Exxon), Magna forming (Engelhard), Catalytic reforming (IFP), Rheniforming (Chevron) and Ultra forming (Amoco). The old technologies are fixed bed configuration. Moving bed technology has also recently been introduced.

1.2.7.1 Semi-regenerative Fixed Bed Process

The schematic flow diagram of this process is shown in Figure 1.5. The name semi-regenerative comes from regeneration of the catalyst in the fixed bed reactors after shut down by burning off the carbon formed on the catalyst surface.

Reactions such as dehydrogenation of paraffins and naphthenes which are very rapid and highly endothermic (Table 1.2) occur in the first reactor, with high temperature drop. Reactions that are considered rapid, such as paraffin isomerization and naphthenes dehydroisomerization, give moderate temperature decline in the second reactor. Furthermore, slow reactions such as dehydrocyclization and hydrocracking (Table 1.2) give low temperature decline in the third reactor.

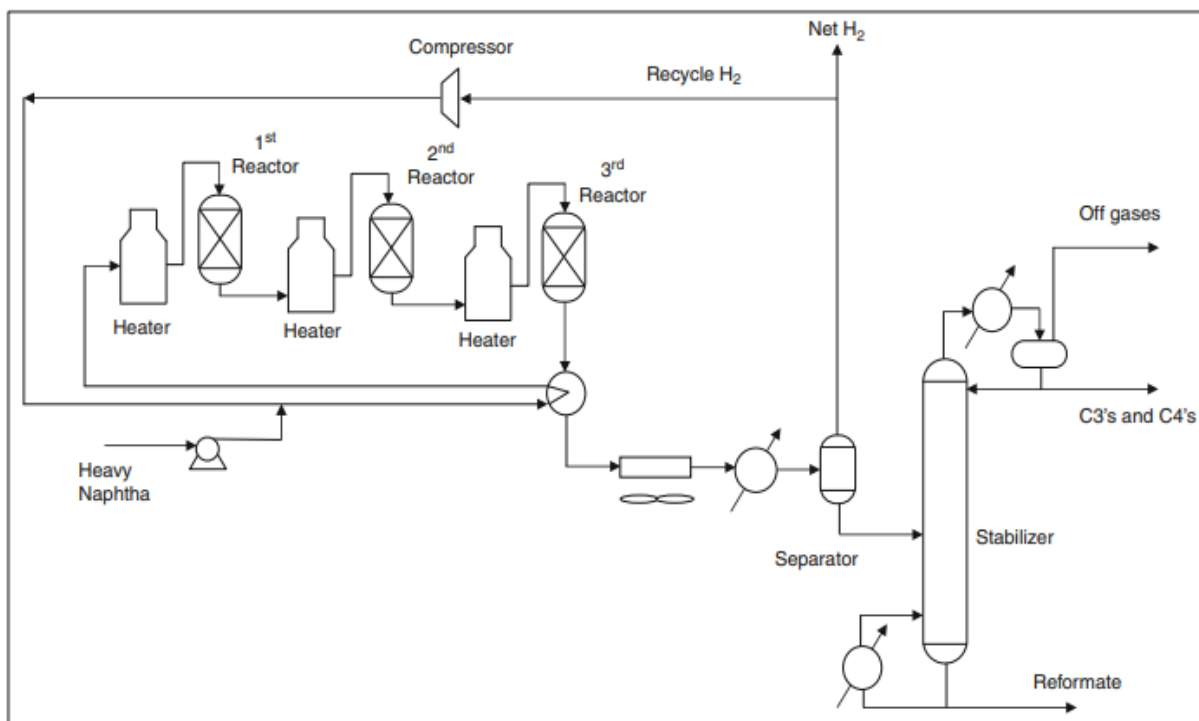


Figure 1.5 Semi-regenerative (SR) fixed bed reforming process

Table 5.1 Thermodynamic and kinetic comparison and effect of operating condition on main reactions and products

Reaction type	Reactive rate	Heat effect	Reaction equilibrium	Pressure effect	Temperature effect	H ₂ production	RVP ^a	Product density	Yield	Octane
Naphthene dehydrogenation	Very rapid	Very endo	Yes	–	+	Produce	–	+	–	+
Naphthene dehydroisomerization	Rapid	Very endo	Yes	–	+	Produce	–	+	–	+
Paraffin isomerization	Rapid	Slight exo	Yes	None	Slight	No	+	Slight –	Slight +	+
Paraffin dehydrocyclization	Slow	Very endo	No	–	+	Produce	–	+	–	+
Hydrocracking	Very slow	exo	No	++	++	Consume	+	–	–	+

^aRVP is Reid vapour pressure.

The temperature and concentration profile in each reactor is shown in Figure 1.6. To prevent catalyst coking, the hydrogen partial pressure is maintained at a level such that the hydrogen-to-hydrocarbon ratio by weight (H₂/HC) is greater than 25 for monometallic catalyst. This is done by recycling some of the hydrogen produced (Figure 5.5). Some light hydrocarbons (C₁–C₄) are separated from the reformat in the stabilizer. At the top of the stabilizer residual hydrogen and C₁ to C₄ are withdrawn as condenser products, which are then sent to gas processing, and part of the liquid product (C₃ and C₄) is returned from the reflux

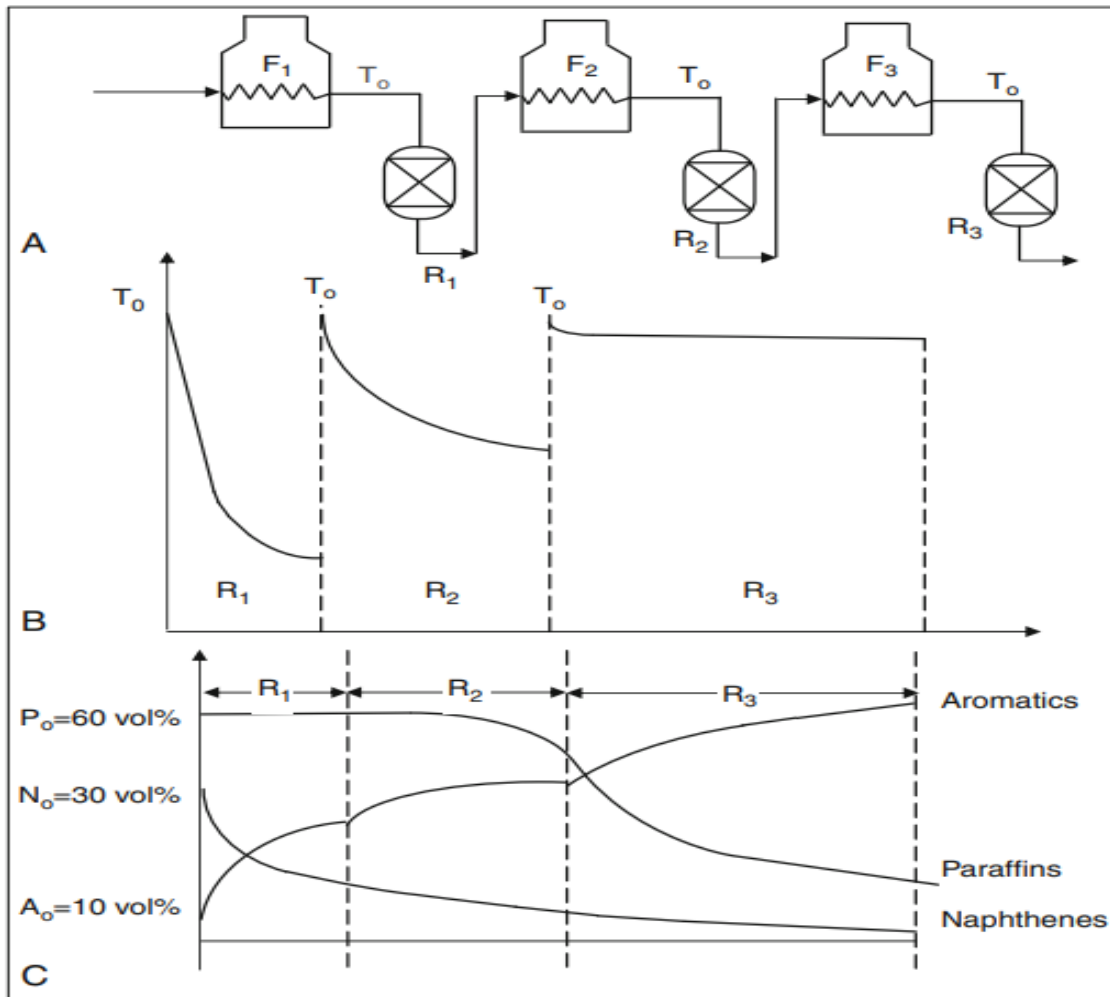


Figure 1.6 (A) Furnace and reactor layout for fixed bed reformer (B) Variation of temperature in the reactors. (C) Variation in effluent compositions; P₀ , initial Paraffins; N₀ , initial Napthenes and A₀ , intial Aromatics

drum back to the stabilizer (Figure 1.6). The main product of the column is stabilized reformat, which is sent to the gasoline blending plant. A slight modification to the semi-regenerative process is to add an extrareactor to avoid shutting down the whole unit during regeneration. Three reactors can be running while the forth is being regenerated. This modified process is called the “cyclic fixed bed” process.

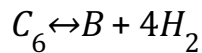
CHAPTER 2

EX.

$$\Delta G = -106.3 \frac{\text{kJ}}{\text{mol}}$$

$$P = 20 \text{ atm}$$

$$T = 796 \text{ K}$$



The Gibbs free energy of a reaction is defined as :

$$\Delta G = -RT \ln(K)$$

Using This equation, The equilibrium constant can be evaluated as:

$$-106.3 = (-0.008314) (796) \ln (K) \longrightarrow K = 9458178.489$$

The equilibrium conversion is calculated as follows

$$\text{Mole of } (C_6) = 1 \text{ bbl} \left(\frac{42 \text{ gal}}{1 \text{ bbl}} \right) \left(\frac{10^6 \text{ cm}^3}{264.17 \text{ gal}} \right) \left(\frac{0.779 \text{ g}}{\text{cm}^3} \right) \left(\frac{1 \text{ mol}}{84.16 \text{ g}} \right) = 1471.63 \text{ mol}$$

$$\text{Mole of } (H_2) = \left(\frac{10,000 \text{ scf}}{1 \text{ bbl}} \right) \left(\frac{1 \text{ mol}}{379 \text{ scf}} \right) (1 \text{ bbl of } C_6) = 26.39 \text{ mol}$$

We will assume “ X ” mols is transformed to (B) and (4X) to (H_2), The equilibrium constant can be expressed as :

$$K = \frac{P_B P_{H_2}^4}{P_{C_6}}$$

The mol fraction of products are:

Mole of (B) = X

Mole of (C₆) = 1471.63-X

Mole of (H₂) = 4X+26.39

Total mole = 1498+4X

The equilibrium constant of be expressed as:

$$K = \frac{(y_B P_T)(y_H P_T)^4}{(y_{C_6} P_T)} \quad \Longrightarrow \quad 9458178.489 = \frac{\left(\frac{X}{1498 + 4X}\right)\left(\frac{4X + 26.39}{1498 + 4X}\right)^4}{\left(\frac{1471 - X}{1498 + 4X}\right)}$$

X=1460.9 mol

This value ((X'')) was extracted by numerical methods using Newton Raphson

$$\text{Equilibrium conversion of (C}_6 \text{)} = \frac{\text{mol of (C}_6 \text{) reacted}}{\text{mol of (C}_6 \text{) feed}} \quad \Longrightarrow \quad \frac{1460.9}{1471.63} =$$

0.992

Table				
Interactions	ΔG	Equilibrium constant (K)	Value of (X)	Conversion

Using the same steps, values were extracted for the other reactions as shown in the table

$C_6 \leftrightarrow B + 4H_2$	-106.3 KJ/mol	9458178.489	1460.900 mol	0.992
$CT \leftrightarrow T + 4H_2$	-93.7 KJ/mol	1409119.789	1407.616 mol	0.956
$C_8 \leftrightarrow X + 4H_2$	-83.0 KJ/mol	279752.192	1224.801 mol	0.832
$C_9 \leftrightarrow 1,3,5MB + 4H_2$	75.4 KJ/mol	88722.300	976.855 mol	0.663
$C_{10} \leftrightarrow Para - cummene + 4H_2$	-71.0 KJ/mol	45633.96	817.022 mol	0.555
$CC_6 \leftrightarrow B + 3H_2$	-78.2 KJ/mol	135450.112	1076.338 mol	0.731
$1,1 - MCC6 \leftrightarrow X + 3H_2$	-69.5 KJ/mol	36379.147	764.565 mol	0.519
$1,3,5 - MCC6 \leftrightarrow 1,3,5 - MB + 3H_2$	-63.9 KJ/mol	15608.435	589.080 mol	0.400
$1,2,3,4 - TMCC6 \leftrightarrow Para - cummene + 3H_2$	-58.3 KJ/mol	6696.782	451.358 mol	0.306
$C_6 + H_2 \leftrightarrow iC_5 + C_1$	-100.5 KJ/mol	3937219.237	1447.147 mol	0.983
$C_7 + H_2 \leftrightarrow iC_5 + C_2$	-92.9 KJ/mol	1248673.493	1400.162 mol	0.951
$C_8 + H_2 \leftrightarrow iC_5 + C_3$	-85.2 KJ/mol	390072.926	1279.225 mol	0.869
$C_{10} + H_2 \leftrightarrow iC_5 + C_4$	-77.6 KJ/mol	123710.084	1055.545 mol	0.717
$C_{10} + H_2 \leftrightarrow 2iC_5$	-72.2 KJ/mol	54706.219	860.085 mol	0.584

